



The role of catalyst in supercritical water desulfurization



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ABSTRACT

We evaluated supercritical water (SCW) for sulfur removal from Arabian Heavy (AH) whole crude oil and two model feeds: hexyl sulfide (HS) in hexadecane (HD) and dibenzothiophene (DBT) in HD. We measured SCW desulfurization performance in the absence and presence of ZnO, MoO₃ and MoS₂. No external hydrogen source, aside from water and oil itself, was added to the reaction mixture. SCW alone (without a catalyst) removes 6–7% of the sulfur present in AH, and addition of MoS₂ improves the sulfur removal by a factor of 2 (to ~12%). For the HS–HD model feed, we found that HS conversion in SCW alone is high (~85%) and is weakly affected by addition of catalysts. Hence, we infer that catalysts have minimal effect on the decomposition rates of aliphatic sulfide compounds. Addition of any of the three catalysts improved the decomposition of DBT in the HD model feed, with ZnO providing the strongest effect (from 3 to 25%). Furthermore, ZnO and MoO₃ catalysts promoted total sulfur removal, indicating a reduction in the formation of secondary sulfur compounds in the presence of oxide catalysts. We characterized the bulk and surface properties of fresh and SCW-exposed catalysts for treatment of the HS–HD model system using X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectrometry (XPS). As anticipated, MoS₂ remained unchanged during the SCW treatment, whereas MoO₃ and ZnO underwent structural and morphological changes primarily related to sulfidation reactions. The results of this work help establish the role of catalysts in the SCW process; demonstrate that modest desulfurization can be achieved in the absence of an external hydrogen source; and provide guidelines for catalyst selection.

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1. Introduction

The removal of sulfur-containing compounds from crude oil is increasingly important due to steady increases in the sulfur content of remaining petroleum resources and mounting environmental concerns associated with SO_x emissions. The primary sulfur removal method is hydrosulfurization (HDS), a process that has long been used at the refinery level [1–3]. Refining high sulfur feeds to meet increasingly stringent sulfur requirements has placed stress on the performance of HDS, especially due to the costs of the large amounts of required hydrogen. For this reason, hydrogen-free sulfur removal processes have received substantial interest in the last decade [4]. Hydrogen-free sulfur removal methods include oxidation desulfurization (ODS) [5–8], oxidation–extraction

desulfurization (OEDS) [9–11], adsorption desulfurization (ADS) [12–16] and bio-desulfurization (BDS) [17–19]. None of the options to HDS has been proven economically viable at commercial scales, motivating continued efforts to identify hydrogen free methods to reduce sulfur content.

Supercritical water (SCW) treatment is a potential sulfur removal technique that is particularly beneficial for treating heavy oils [20–24]. SCW is a good solvent for promoting heteroatom removal, as both C–O (as in ethers) and C–S bonds (as in sulfides) are cleaved more easily in SCW than they are under conventional “dry” pyrolysis conditions [25–31]. Furthermore, SCW is a non-polar solvent that has the ability to dissolve organic compounds, which includes the majority of components in crude oil, as well as “permanent gases”. In certain cases, reaction rates and product distribution in reactions performed in SCW can be manipulated by adjusting reaction conditions, e.g., temperature, pressure, reactants concentration, and catalysts [32]. SCW has a viscosity comparable to a gas, which accelerates mass transfer processes relative to their liquid phase rates and allows some catalysts to retain high activity for extended periods of time [25,32,33]. However, SCW is a

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chemically aggressive environment, which can rapidly de-activate many catalysts, so they must be selected carefully [34–38].

Upgrading heavy oils using SCW has been described in a few U.S. patents, which claim that the process can be performed without addition of catalysts or external hydrogen sources [39–41]. Lin et al. [39] used SCW in the absence of an external hydrogen source, without a catalyst, to upgrade hydrocarbons and obtained products with highly desirable properties, such as low sulfur and metal contents, lower density and viscosity, and lower residuum contents. In a similar study, Choi and Al-Shareef used an ultrasonic wave generator and hot pressurized water to upgrade Arabian heavy crude oil [40]. In contrast, a SCW process reported by Banerjee to upgrade extra heavy crude oil required addition of either hydrogen or CO and the presence of an alkali-salt promoted zirconium or iron oxide catalyst [41]. A landmark academic study on the desulfurization and de-metalization of gas oil in SCW showed that, without addition of hydrogen and catalysts, SCW is not sufficient for upgrading sulfur-spiked gas oil [42]. Furthermore, Adschiri et al. [43,44] have systemically investigated the hydrothermal cracking of dibenzothiophene (DBT) in SCW in the presence of NiMo catalysts at pressures and temperatures as great as 30 MPa and 703 K, respectively. They found that desulfurization required the addition of a hydrogen carrier such as molecular hydrogen, CO, CO₂/H₂, or HCOOH.

The literature discrepancies on the effectiveness of the SCW process may be due in part to differences in the sulfur compounds that were studied by the different research teams. Indeed, different sulfur group types respond differently to the SCW process. Non-aromatic sulfur compounds, including sulfides and thiols, cleave easily in SCW, whereas, compounds with sulfur in an aromatic ring are more stable [20,28,29]. Therefore, SCW desulfurization of aromatic sulfur compounds may require addition of either a catalyst or other additives [42,43,45]. However, because of the poisoning effect of sulfur for metal catalysts, aggregation and dissolution of solid materials, and oxidation of metal components in SCW, only a limited range of catalytic materials can be used in the process [36,46,47]. In addition, conventional catalyst support materials, such as silica and alumina, severely degrade in the SCW reaction environment [46]. Catalyst stability under SCW conditions has been the focus of only a handful of studies, most of them focused on biomass gasification conditions [37,48,49] rather than sulfur removal conditions relevant to petrochemical processes [34–36,46]. In SCW gasification studies, three types of heterogeneous catalysts, including activated carbon, transition metals, and their oxides, have been used to promote SCW gasification [37,48]. In particular, the oxides of Ce, Co, Fe, Mn, Ti, Mo, and Zn have been commonly used as catalysts in SCW [47].

In this work, we studied the effect of several low-cost catalysts on SCW desulfurization of three types of sulfur-containing feeds, including Arabian heavy crude oil and hexadecane (HD) mixtures of hexyl sulfide (HS) and dibenzothiophene (DBT), in the absence of an external hydrogen source. We evaluated MoS₂, a traditional HDS catalyst; MoO₃, the oxide of an HDS catalyst; and ZnO, which is an H₂S adsorbent that has been used for reactive adsorption of sulfur. These catalysts were tested for activity, stability, and chemical mechanism elucidation.

2. Experimental

In their reviews of heterogeneous catalysis in SCW, Savage [38] and later Yeh et al. [37] cited a need for greater understanding of the catalyst stability, including morphological changes that occur in SCW at different conditions. Moreover, the SCW upgrading of crude oil is particularly challenging given that the catalyst must be stable in the presence of water and sulfur, both of which degrade the catalyst but via different mechanisms. Much of our knowledge

on catalyst stability in SCW is from the work on SCW gasification [50] on low-sulfur biomass feeds, as reported originally by Pacific Northwest National Laboratory [49]. For this reason, a study that probed catalyst stability at SCW conditions in the presence of a sulfur rich feed was needed. We selected 3 materials for our preliminary study – MoS₂, MoO₃, and ZnO. Each of these materials is available at low cost; Table 1 explains the selection of each material and some of their properties. Conveniently for purposes of comparison, the initial BET surface areas and pore volumes of the catalysts were similar to one another, all in the range from 7 to 10 m² g^{−1} and 0.041 to 0.052 cm³ g^{−1}, respectively. In terms of expected performance, MoS₂ is a known HDS catalyst, whereas ZnO is a known H₂S adsorbent. H₂S has well documented effects on chemical reactivity [51] and we were interested if H₂S removal might alter SCW desulfurization. Moreover, we wanted to investigate 1) the influence of H₂S removal on the formation of “secondary” sulfur compounds and 2) the use of ZnO as a “co-catalyst” to protect a second, more active catalyst from H₂S poisoning. Finally, MoO₃ was selected as a sulfur adsorbent that would be sulfided into a form with potential catalytic activity (MoS₂). Previous work had shown that sulfidation of MoO₃ produced a high-surface-area MoS₂ that might prove to have high catalytic activity [52–55].

To study both sulfur- and water-rich conditions, we investigated catalyst performance and stability for three feeds: 1) Arabian Heavy (AH), 2) model hexadecane oil containing 3 wt% hexyl sulfide (HS-HD), and 3) model hexadecane oil containing 0.1 wt% DBT (DBT-HD). Table 2 summarizes the experiments and their selection rationale. Arabian Heavy was selected to test performance for a real feed with high sulfur content. DBT-HD was selected because DBT is well known to be highly refractory to HDS and is present in modest quantities in AH. However, because the solubility of DBT in HD at room temperature is low, we studied a 0.1 wt% solution (on a sulfur basis). HS-HD was selected to re-produce the high sulfur conditions present for treatment of AH. Additionally, HS-HD is known to decompose rapidly to produce H₂S in near- and SCW to yield H₂S [27,56] and we were particularly interested in probing the effects of H₂S on catalyst stability without the hazards of handling and storing pressurized H₂S cylinders.

2.1. Materials

Di-n-hexyl sulfide (HS, 97% purity) and dibenzothiophene (DBT, 99% purity) were purchased from Alfa-Aesar and Aldrich, respectively. Hexadecane (HD, 99% purity) was purchased from Sigma-Aldrich. The catalysts were obtained from Sigma-Aldrich: zinc oxide (ZnO, ACS reagent, ≥99.0%, p/n 251607), molybdenum (VI) oxide (MoO₃, ACS reagent, ≥99.5%, p/n 267856), and molybdenum (IV) sulfide (MoS₂, powders with particle size of ~6 μm, p/n 69860). Arabian heavy (AH) crude oil was obtained from Saudi Aramco Company. Table 3 lists some relevant characteristics of the feed [57]. SARA (Saturates-Aromatics-Resins-Asphaltenes) analysis was performed using an HPLC technique, similar to that published in the literature [58]. All chemicals were used without further purification. Water was de-ionized (DI) to a resistivity of 18.1 MΩ cm immediately prior to use.

2.2. Apparatus and reaction runs

All runs were carried out in a 316-stainless steel batch microreactor (24 ml in volume) obtained from High Pressure Equipment Company (p/n MS-16) and equipped with a 316-stainless steel cross for connecting the reactor to a pressure transducer, a gas feed/collection port, and a rupture disk for safety. Heating was provided by a fluidized sand bath (Techne Industrial, p/n FB-08) with a temperature control precision of ±0.5 °C. For all runs, temperature

Table 1
Selection and surface characteristics of materials.

Material	Selection criteria	Original sample			Tested sample		
		SA ^a (m ² g ⁻¹)	V _T ^b (cm ³ g ⁻¹) 10 ²	D ^c (Å)	SA ^a (m ² g ⁻¹)	V _T ^b (cm ³ g ⁻¹) 10 ²	D ^c (Å)
MoS ₂	Well known HDS catalyst	9.8	5.2	229	11.6	6.1	209
ZnO	Well known H ₂ S adsorbent	9.7	4.1	168	17.6	8.1	184
MoO ₃	Predicted to become sulfided in the presence of H ₂ S to form MoS ₂	7.3	4.2	230	13.8	7.6	220

^a Surface area calculated using Multipoint BET.^b Total pore volume calculated at 0.99 of P/P₀.^c Average pore diameter.**Table 2**
Composition and selection rationale of feeds for SCWD.

Feed	Composition	Selection rationale
Arabian Heavy	See Table 3	Real feed with high sulfur content and low metal content
HS-HD	3 wt% hexyl sulfide (as sulfur) in hexadecane	High sulfur model feed that produces H ₂ S during decomposition
DBT-HD	0.1 wt% dibenzothiophene (as sulfur) in hexadecane	Model feed containing DBT as a refractory sulfur compound

was maintained at 400 °C. The reaction pressure was always between 23 and 33 MPa, with a typical starting value being 25 MPa.

For tests with model feeds, solutions of HS-HD, containing 3 wt% S, DBT-HD, containing 0.1 wt% S, and AH crude oil, were prepared. Around 3.5 g of the hydrocarbon/sulfur mixture and DI water at a 1:1 weight ratio were loaded into the reactor. Control runs were performed in the absence of catalyst to ascertain the effects of SCW on sulfur removal from AH and model feeds. For the runs with added catalyst, ~0.35 g of the catalyst was added to the reactor along with the water and hydrocarbon feed. SCW of AH crude oil was performed under the same conditions as the model feeds (3.5 g of crude oil, 3.5 g of water and 0.35 g of catalyst). Prior to each test, air in the reactor and reactor connections was removed by purging with He gas multiple times. He gas was then added to the reactor (at approximately 2 MPa) to prevent formation of liquid phases of either water or hydrocarbon in the cool line leading to the pressure transducer. Control experiments using water only indicated that final pressures could be predicted using the steam tables when pressurized helium was used to fill the pressure transducer and

associated tubing. Without helium, we found that the steam tables under-predicted the final reactor pressure, indicating that a liquid water phase had formed in the transducer and tubing. After He pressurization, the reactor was submerged into the fluidized sand bath. Temperature measurements on control runs indicate that the reactor reaches 90% of its final temperature within 5 min. The pressure of the reactor was monitored using a pressure transducer (Omega Engineering, 0–33.6 MPa) and logged on a computer. The final pressure achieved after heating was always greater than the critical pressure of water (21.8 MPa). After a pre-determined reaction time (30–60 min), the reactor was removed from the sand bath and rapidly quenched in a cold-water bath.

The reactor was not mixed during reaction. Wu et al. [59] suggest that hexadecane–water system should form a 1-phase mixture at 400 °C and 25 MPa. Amani et al. [60] performed tests on bitumen/water phase behavior at temperatures up to 380 °C and pressures up to 30 MPa. Based on the Amani et al. [60] data, we conclude that the Arabian Heavy–water mixture consisted of two liquid phases in equilibrium. Phase behavior and mixing may influence reactivities and sulfur removal performance and we are currently re-designing a tubular flow reactor for performing experiments with Arabian Heavy under flow conditions.

Table 3
The characteristics of Saudi crude oil.

Elemental analysis			
Sulfur	3.0 wt%		This study
Nitrogen	0.16 wt%		[57]
Vanadium	69 ppm		[57]
Nickel	21 ppm		[57]
Saturates–Aromatics–Resins–Asphaltenes (SARA) analysis (for boiling point >200 °C)			
Fraction	wt% recovered	wt% sulfur	This study
Saturates	22	0.0	This study
Aromatics	49	4.3	This study
Resins	15	4.8	This study
Asphaltenes	14	5.4	This study
Gravity, °API		28.1	[57]
Atmospheric distillation analysis			
Fraction	wt% recovered	wt% sulfur	This study
<150 °C	2.2	<50 ppm	This study
<200 °C	2.2	<50 ppm	This study
<250 °C	8.1	0.26	This study
<300 °C	6.6	0.64	This study
<350 °C	10.6	1.18	This study
<400 °C	22.4	2.44	This study
<450 °C	29.2	4.06	This study
Residual	18.7		This study

2.3. Analysis

After quenching the reactor, all products (i.e., gas, hydrocarbon and water) were characterized. Gas phase products were collected in a Tedlar bag gas collection and injected into either a gas chromatograph (GC) or gas chromatograph–mass spectrometer (GC–MS) using a gas-tight syringe. To quantify sulfur-containing products, we used a gas chromatograph (GC, Shimadzu model 2014) equipped with an RTX-1 column (30 m, 0.32 mm ID, 4 μm film thickness) and a sulfur chemiluminescence detector (SCD, Agilent, model 355). To quantify carbon-containing products in the gas phase, we utilized a GC (Shimadzu, model 2014) equipped with a RT-Q-bond column (30 m, 0.53 mm ID) and a flame ionization detector (FID). To identify gas phase products (e.g. CO₂, C₂H₄, H₂S, C₃H₆, C₃H₈, C₃ H₆, H₂O, C₄H₁₀, C₄H₈, SO₂, SCO, etc.), we used a GC (Agilent, p/n 5890) equipped with a mass selective detector (Agilent, p/n 5972) and an RT-S-bond column (30 m, 0.25 mm ID, 0.25 μm film thickness). The total gas product was quantified by comparing the final and initial reactor pressures and using the ideal gas law to convert the pressure increase to the number of moles of the gas product.

After reaction quenching, the oil and water formed an emulsion that was separated by centrifugation at 6000 rpm at room

temperature for 30 min. For tests with AH crude oil, a demulsifier (1% (v/v) of total liquid) was added to the water–oil mixture before centrifugation to promote phase separation. The recovered oil phase was analyzed using: a GC/SCD (Shimadzu model 2014 and Agilent model 355) equipped with an RTX-1 column (30 m, 0.32 mm ID, 4 μ m film thickness); a GC (Agilent model 6890) equipped with a mass selective detector (Agilent model 5975) and an HP-5MS column (30 m, 0.25 mm ID, 0.25 μ m film thickness); and a Horiba XRF (model SLFA-1800H) for total sulfur content. The conversion of sulfur containing compounds, HS and DBT, was calculated by comparing the GC/FID peaks areas in the feed and the oil product.

A representative subset of the water phase samples collected after SCW treatment were analyzed for elemental content using proton induced X-ray emission (PIXE, performed by Elemental Analysis, Inc.).

2.4. Catalysts characterization

To determine stable phases and their crystallographic structures, fresh and used catalysts were characterized using X-ray diffraction, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and nitrogen sorption. Only the most pertinent information on these methods is provided here; the Supporting Information provides detailed procedures for each method. X-ray diffraction over 2θ angles of $10\text{--}70^\circ$ (XRD, PANalytical X'Pert Pro Multipurpose Diffractometer with X'Celerator position sensitive detector and Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$)). To obtain the surface morphology, microstructural characterization of fresh and used catalysts was performed using scanning electron microscopy (SEM, JSM-6610LV) at an accelerating voltage of 20 kV. To determine the surface chemistry, fresh and used catalysts were characterized by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics Versaprobe II X-ray photoelectron spectrometer (LS) with a base pressure of 1×10^{-10} Torr. The specific surface area and pore characteristics of the samples were measured using N₂ adsorption–desorption (AUTOSORB 1C) at -196°C . The surface area and pore volume were determined by multipoint BET and DFT (Density functional theory), respectively.

2.5. Theoretical approach

To complement experimental investigation of catalyst phase stability, we modeled the thermodynamic behavior of the water–oil–catalyst systems using OLI Systems software. The OLI software uses the HKF model, developed by Tanger and Helgeson [61], to extrapolate the standard state thermodynamic properties to high temperatures and pressures. The initial mixture composition consisted of water (87 mol%), hexadecane (7 mol%), CO₂ (3 mol%), H₂S (1.5 mol%), hexane (1 mol%), pentene (1 mol%), in contact with the catalyst. Further details are provided in the Supporting Information. For all cases, modeling results were in good agreement with the experimental observations.

3. Results and discussion

3.1. SCWD of AH crude oil with and without MoS₂ catalyst

To study the effectiveness of SCW for the desulfurization of heavy oil, we treated AH crude oil in SCW for up to 60 min at 400°C and 25 MPa without catalyst as a control. We then used MoS₂ to investigate the effect of adding catalyst on the process efficiency. SCW treatment alone resulted in modest sulfur removal (6–7%) of the crude oil as measured by XRF on the oil fraction. Addition of MoS₂ promoted the sulfur removal by a factor of 2 up to $\sim 12\%$, as shown in Fig. 1.

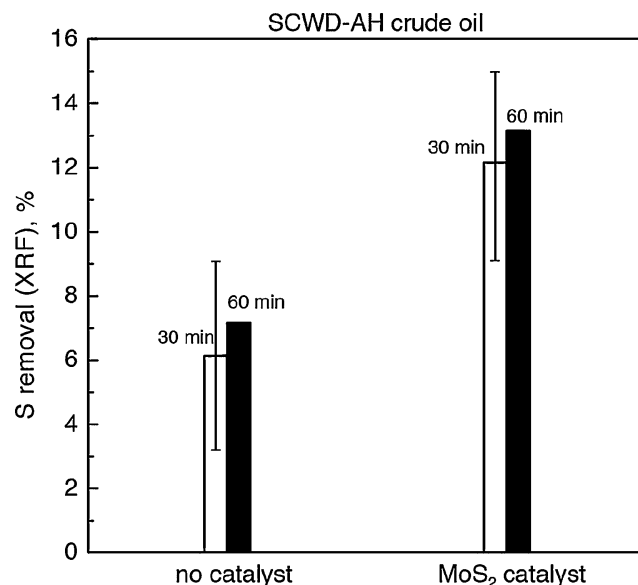


Fig. 1. Sulfur removal from AH crude oil in SCW at 400°C and 25 MPa with and without MoS₂ as a catalyst.

The experimental procedure gives total XRF values that are reproducible to within $\pm 3\%$ leading to the error bars shown. Total sulfur measurements by XRF alone provide evidence for SCW desulfurization that is scarcely above our estimated detection limits. However, more detailed analysis of the hydrocarbon and gas products supports the conclusion that AH is desulfurized in the SCW treatment and that addition of MoS₂ improves desulfurization performance. Analysis of the liquid hydrocarbon product using GC–SCD showed that H₂S was formed, and some of the H₂S remained in the treated AH (see Fig. 2), which is consistent with H₂S absorption in the crude oil. This implies that total sulfur removal from AH could be improved by removing residual H₂S, as could be achieved in

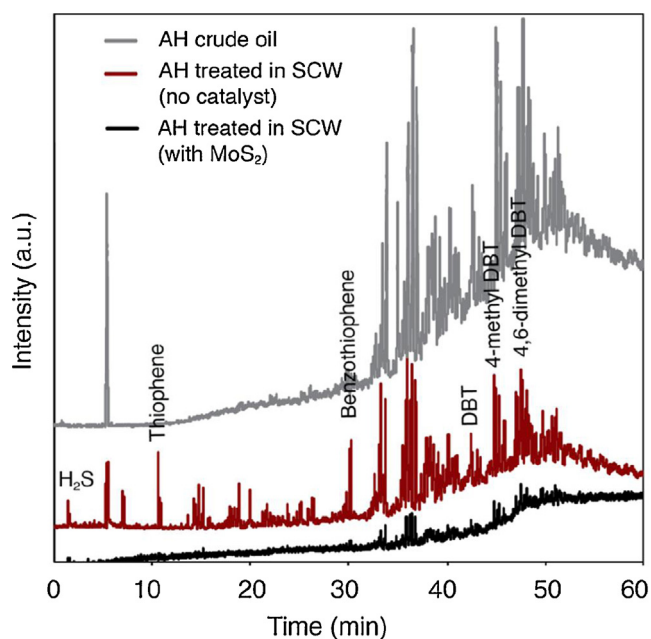


Fig. 2. Sulfur containing product distribution formed during SCWD of AH crude oil with and without a catalyst at 400°C and 25 MPa for 30 min [Feed: 3 wt% S (crude oil) (3.5:3.5 wt/wt of oil/water at room temperature)].

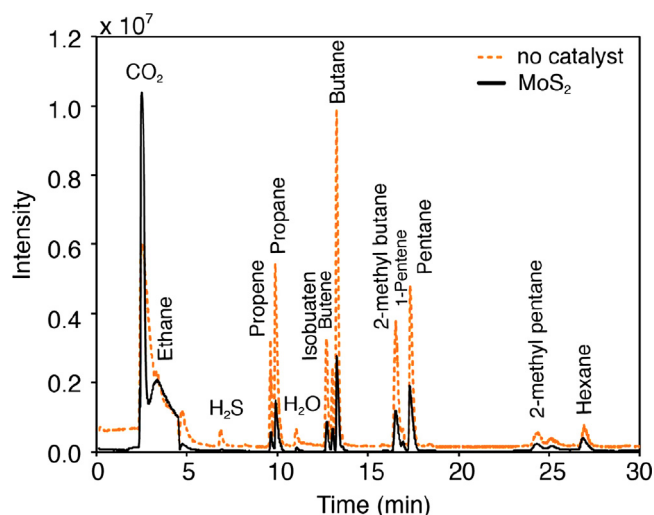


Fig. 3. Gas product distribution, based on total ion content measured by GC–MS formed during SCW desulfurization of AH crude oil at 400 °C and 25 MPa for 30 min with and without MoS₂ catalyst [Feed: 3 wt% S (crude oil) (3.5:3.5 wt/wt of oil/water at room temperature)].

the laboratory using a helium purging procedure or as would be performed industrially using distillation or flashing operations

Fig. 2 indicates that SCW treatment of AH increases the concentration of volatile sulfur compounds that elute from the GC prior to 15 min. Based on their retention times compared to known standards, we attribute these new peaks to a combination of thiophenes, sulfides, and thiols. Additionally, Fig. 2 shows that the benzothiophene and dibenzothiophene content of the AH shifts during the SCW treatment. Interestingly, the SCW treatment greatly increases the concentrations of certain compounds – chiefly benzothiophenes – while decreasing the concentrations of others. Relative to the control performed in the absence of catalyst, Fig. 2 shows that the MoS₂ treated AH sample had lower thiophenic sulfur content. Identification of H₂S in the AH product and the shift in the sulfur compound distribution clearly show that sulfur compounds react during the SCW process. Because AH has low metals content (see Table 3), we conclude that the metal content native to AH cannot fully explain the sulfur chemistry evidenced in Fig. 2.

Analysis of the gas product indicated the presence of H₂S, further evidence of AH desulfurization under SCW conditions. Surprisingly, MoS₂ reduced the H₂S content of the gas product, despite the improved sulfur removal performance of MoS₂ relative to SCW alone. Additionally, the AH gas products contained C₂–C₆ hydrocarbons that were not present in the feedstock (see Fig. 3), consistent with SCW-promoted cracking of the AH. In addition to the hydrocarbons, the AH gas products also contained CO₂. Considering that the reactor was purged of O₂ before running the reaction and that water was the only source of oxygen in the system, detecting CO₂ in the gas product implies that water participates in the reaction. Formation of CO₂, rather than CO, suggests that the reactor wall (and potentially also the MoS₂) may promote the water–gas-shift (WGS) reaction.

We analyzed representative water phase samples obtained after the SCW desulfurization treatment of AH using PIXE. After treatment of AH, the water phase contained ~100 ppm_w sulfur, but we were not able to determine its molecular form. The most likely explanation is that H₂S dissolved into the water and the aqueous H₂S oxidized to colloidal sulfur during storage. Few studies have reported the formation of sulfur and its compounds during SCW desulfurization: Lachance et al. [62] have observed direct formation of elemental sulfur from SCW decomposition of thiodiglycol;

Adschiri et al., have reported formation of sulfite during their tests of SCW desulfurization in the presence of additives [43,44].

Although PIXE is sensitive to all atoms with atomic number greater than 11 (Na), except for noble gases and some rare-earth elements, with a sensitivity detection limit greater than 1 ppm_w, it did not indicate any catalyst components (e.g., Mo) or reactor wall elements (e.g., Fe, Cr, and Ni) in the water phase obtained after SCW desulfurization treatment of the AH feed. This is an important finding given that H₂S can cause corrosion of certain materials, resulting in catalyst deactivation and reactor failure [63,64]. Based on the PIXE characterization of the water product, we conclude that 316-stainless steel is compatible with the SCW-AH environment, despite the sulfur and metals content of AH. Additionally, the PIXE result strongly suggests that our SCW desulfurization results cannot be ascribed to homogeneous catalysis from catalyst or reactor wall corrosion products [65], though we cannot rule out potential surface catalytic effects of the reactor walls themselves.

The SCW desulfurization of AH crude oil yielded some promising results: some sulfur reduction was observed in the absence of an external hydrogen source. However, due to the low volatility of AH, only about 25% of total sulfur content of the AH can be analyzed using our GC technique. Therefore, interpretation of changes in the benzothiophene and dibenzothiophene content (shown in Fig. 2) must take into account cracking of larger compounds, which are not originally detectable by GC in the AH stock, into smaller ones that become GC detectable after the SCW treatment, and for the decomposition of the observed compounds. Hence, to understand the role of catalysis on SCW desulfurization, we performed a series of additional tests with model sulfur compounds.

3.2. SCW treatment of model feeds

As described in Table 3, we studied two different model feeds: hexyl sulfide (HS) as a 3 wt% solution (by sulfur) in hexadecane (HD) and dibenzothiophene (DBT) as a 0.1 wt% solution (by sulfur) in HD. The concentration of HS was selected to simulate the sulfur content of AH crude oil. The DBT concentration was limited by its much lower solubility in HD. To study the effect of catalysts, we performed SCW desulfurization in the presence of MoS₂, MoO₃, and ZnO catalysts. Table 1 provides the rationale for selection of these 3 materials.

3.2.1. The HS-HD model feed

The SCW desulfurization results of total sulfur removal (measured by XRF) and HS decomposition (measured by GC-FID) for the HS-HD model system with and without a catalyst after 30 min and 60 min, are shown in Fig. 4a and b, respectively. The uncertainty in residual HS measurements was estimated to be less than 5%, based on replicate runs. In the absence of a catalyst, SCW alone, with 30 min residence time, resulted in 90% HS conversion. As we would expect for a non-equilibrated reaction, increasing the reaction time to 60 min resulted in an increase in HS conversion (see Fig. 4a and b).

As we anticipated (see Section 2), neither ZnO nor MoO₃ influenced HS decomposition, whereas MoS₂ only modestly improved HS decomposition. HS is already known to react in SCW at these conditions, making addition of a catalyst unnecessary. Furthermore, results from ZnO and MoO₃ indicate that H₂S liberated during HS decomposition plays only a minor auto-catalytic role. The effects of catalysts on formation of secondary sulfur compounds are more interesting. Fig. 4a and b show that total sulfur removal from the HS-HD model feed (measured using XRF) was less than its decomposition, measured using GC/FID, a result that is consistent with formation of secondary sulfur compounds that retain oil solubility. The difference between total sulfur removal and HS decomposition for MoS₂ was less than the two other catalysts, consistent

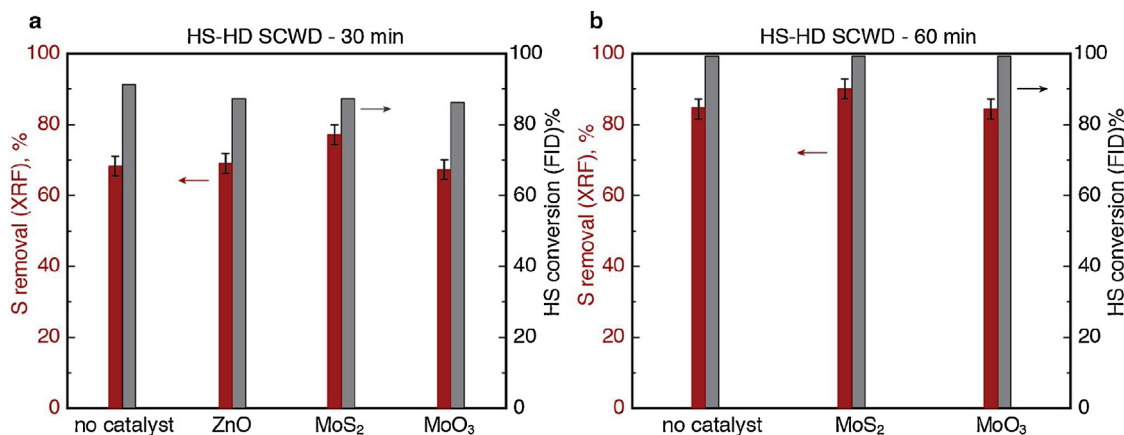


Fig. 4. (a and b) Desulfurization of HS-HD model feed in SCW with and without a catalyst at 400 °C and 25 MPa for 30 min and 60 min, respectively [Feed: 3 wt% S (HS) in HD (1:1 wt/wt of oil/water at room temperature)].

with MoS₂ reducing the formation of secondary sulfur products relative to the MoO₃ and ZnO catalysts and un-catalyzed reaction. Because MoO₃ and ZnO do not reduce formation of secondary sulfur compounds, we conclude that H₂S plays only a modest role in the mechanism to form secondary sulfur compounds. Instead we infer from the MoS₂ result that reducing the formation of secondary sulfur compounds is better achieved either by altering the mechanism to promote HS decomposition into H₂S directly – or into compounds that in turn are decomposed into H₂S.

GC-SCD analysis of the liquid phase products (Fig. 5) and GC-MS analysis of the gas phase products (Fig. 6) support the conclusion that MoS₂ promotes direct decomposition of HS into H₂S more effectively than the other catalysts. Fig. 5 shows GC-SCD evidence that HS decomposes partially into secondary sulfur compounds that were identified as hexane thiol and 5-member rings bearing sulfur using mass spectrometer fragmentation patterns and comparison with the retention times of known standards. Fig. 5 shows that MoS₂ reduces the formation of hexane thiol relative to the non-catalyzed case, though formation of the cyclic sulfides is not altered by the presence of MoS₂. Fig. 6 shows GC-MS results obtained by analyzing the gas product collected after SCW treatment of HS-HD model feeds. In all cases, the primary gas phase products were CO₂,

H₂S, SO₂, SCO, CS₂ as well as propene, propane, butane, butene, pentane, and pentane with H₂S being the dominant gas phase sulfur product. Formation of sulfur containing gases such as H₂S, SO₂, SCO and CS₂, was increased in the presence of MoS₂ catalyst, consistent with the results obtained by analyzing the liquid (hydrocarbon) phase products. Based on these results, we conclude that the H₂S adsorbent materials (ZnO and MoO₃) do not influence HS reactivity, decomposition mechanism, or formation of secondary sulfur products; but, that MoS₂ reduces formation of secondary sulfur compounds – presumably by eliminating the formation of hexane thiol or accelerating its decomposition.

3.2.2. The DBT-HD model feed

Fig. 7 presents the results obtained for SCW desulfurization of the DBT-HD model feed with and without addition of a catalyst. In the absence of a catalyst, sulfur removal from the DBT-HD feed was significantly lower than that of the HS-HD feed, ~1% after 30 min and 3% after 60 min, both so low that we cannot say with confidence that there was any sulfur removal. DBT conversion, however, was higher than expected in the absence of a catalyst, reaching 10% after 60 min of SCW treatment. Addition of a catalyst increased DBT conversion relative to the control, with ZnO

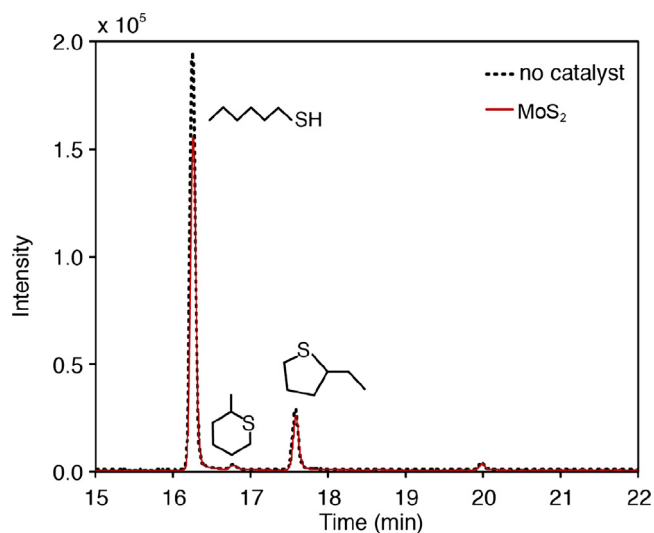


Fig. 5. GC-SCD analysis of the HS-HD hydrocarbon product. Conditions: 400 °C and 25 MPa for 30 min in the absence of a catalyst. Feed: 3 wt% S (HS) in HD (1:1 wt/wt of oil/water at room temperature).

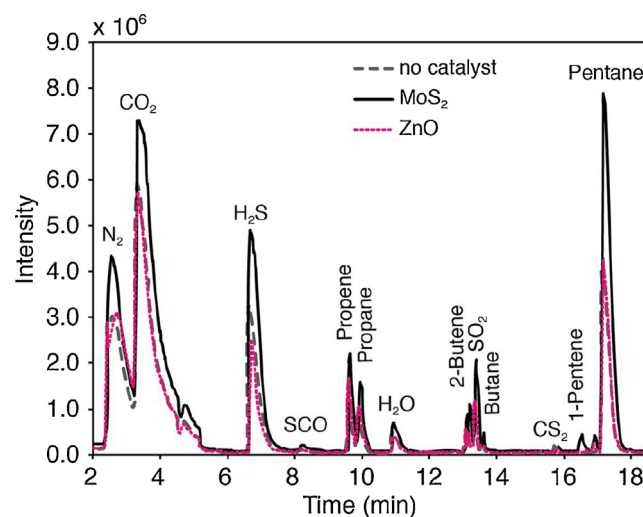


Fig. 6. Gas product distribution after desulfurization of HS-HD model feed in SCW for 30 min with and without a catalyst (MoS₂ and ZnO are shown). Temperature and pressure were set at 400 °C and 25 MPa, respectively [Feed: 3 wt% S (hexyl sulfide (HS)) in hexadecane (1:1 wt/wt of oil/water at room temperature)].

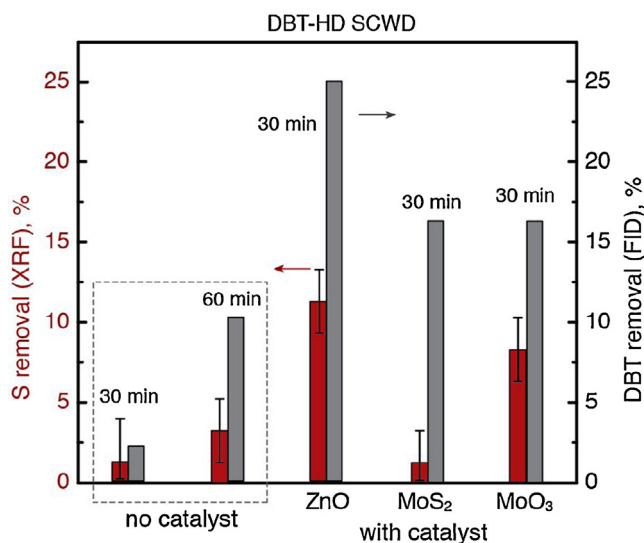


Fig. 7. Desulfurization of DBT-HD model feed in SCW at 400 °C and 25 MPa with and without a catalyst for 30 min. To show the effect of reaction time, the control with no catalyst was tested for 60 min [Feed: 0.1 wt% dibenzothiophene (DBT) in hexadecane (1:1 wt/wt of oil/water at room temperature)].

providing the strongest effect (see Fig. 7). Furthermore, ZnO and MoO₃ catalysts promoted total sulfur removal as well as DBT decomposition, indicating a reduction in the formation of secondary sulfur compounds in the presence of these two catalysts. MoS₂ catalyst was less effective than either ZnO or MoO₃ at removing sulfur from the DBT-HD feed. Decomposition of DBT in the absence of added hydrogen is potentially an important result that is broadly consistent with the observations from the AH experiments. To understand the mechanism, we analyzed the liquid and gas products obtained from SCW-treatment of the DBT-HD feed. Consistent with decomposition of carbon-sulfur bonds, we were able to observe H₂S in the product gas. Unfortunately, due to the low solubility of DBT in the HD phase and the low conversions observed, we could not be quantitative and could therefore not close the sulfur balance. Moreover, we could not detect any of the expected DBT decomposition products in the liquid product (e.g., biphenyl) at concentrations sufficient to explain the disappearance of DBT.

Based on the observation of the H₂S product gas, we conclude that DBT must be decomposing via catalyzed reaction in the SCW solvent. Moreover, the GC/SCD data shown in Fig. 5 clearly show transformations of the dibenzothiophene content present in AH. While we cannot conclusively rule out DBT adsorption onto the “catalyst” surfaces, an engineering comparison with tailored adsorbents suggests that adsorption is likely a minor contribution. In their review of thiophene adsorption, Hernandez-Maldonado and Yang [66] reported that “standard” adsorbents, including several oxide materials, exhibited less than 1 wt% thiophene adsorption capacity. Similarly, Baeza et al. [15] found that ZrO₂ supports have negligible DBT adsorption capacity. Only after addition of Cu or Ag – transition metals known to participate in π - π interactions with thiophenic sulfur [66] – is DBT adsorption on support materials like zeolites or oxides observed [15]. The Philips S-Zorb process reportedly uses a ZnO sorbent [66] to promote sulfur removal. Unlike the SCW process, the S-Zorb process requires an HDS catalyst and external hydrogen [67,68]. Most likely, the ZnO in the S-Zorb process removes H₂S as it forms, preventing further reaction or catalyst poisoning. Despite our confidence in DBT reactivity, we acknowledge this crucial issue and we anticipate performing additional experiments in the future to examine DBT decomposition more closely.

3.3. Characterization of catalysts

Improved understanding of catalyst stability and morphological changes has been cited as a need for developing catalytic SCW technologies [37,38]. Catalyst characterization after exposure to SCW crude oil upgrading conditions, which simultaneously expose the catalysts to a water-rich environment and H₂S, is specifically lacking. To understand better the stability and relative activity of the catalysts, we characterized the surface chemistry, surface morphology and crystallographic structure of fresh and SCW-exposed catalysts, using XPS, SEM, XRD, and nitrogen sorption analyses. We focused on the catalysts that were used for the HS-HD model feed because desulfurization was greatest for this system, therefore exposure to H₂S was highest. In addition, we simulated the chemistry of the system using OLI software to predict catalyst thermodynamic stability under the SCW conditions. Here, we focus on the most relevant composition and morphological changes that occurred during exposure to SCW desulfurization conditions. Table 1 summarizes the results of nitrogen sorption tests, and the Supporting Information contains complete XPS, SEM, and XRD results. In all cases, simulations were in close agreement with experimental observations of phase stability.

3.3.1. Characterization of MoS₂

Among the three catalysts tested, only MoS₂ was found to be stable during SCW treatment of HS-HD. SEM micrographs of MoS₂ before and after SCW treatment of HS-HD are presented in Fig. 8a and b, showing that MoS₂ morphology and size remain unchanged during the SCW treatment. Fig. 8c shows the XRD spectra of MoS₂ before and after SCW treatment of the HS-HD feed for 30 min and 60 min. Based on comparison of our spectra with literature interpretations [69–71], XPS characterization of fresh and the SCW-exposed MoS₂ (30 min) found the surface to contain only Mo, S and C. The presence of carbon after the SCW treatment is suggestive of coke formation and, consistent with this hypothesis, the MoS₂ sample exposed to AH contained (a readily coking feedstock) more carbon than did the HS-HD sample (a feedstock that is less prone to coking). More surprisingly, we found that the surface contained approximately 40% carbon even before the SCW treatment. Supporting temperature programmed oxidation analysis of the fresh MoS₂ sample confirmed the presence of carbon, but we have not yet confirmed the source. Nonetheless, the qualitative results are consistent with catalyst coking in the presence of hydrocarbon feeds and – since catalyst coking is a potential de-activation mechanism – this remains a topic of on-going interest.

3.3.2. Characterization of MoO₃

As anticipated and consistent with simulations, the MoO₃ sample became sulfided during exposure to the HS-HD conditions. Based on the XRD spectra, fresh MoO₃ has an orthorhombic crystal structure; after SCW treatment and exposure to organic sulfur, MoO₃ was converted into MoO₂ and MoS_{0.12}O_{1.88} with a monoclinic crystal structure. These results are consistent with a previous study where the conversion of MoO₃ into MoO₂ and MoS_{2-x}O_x phases has been reported [70]. Likewise, XPS analysis (not shown here) indicated the presence of sulfur (3 atom%) and S/Mo (0.4 atom%) on the used MoO₃ surface. Fig. 9a–c show SEM micrographs of this catalyst before and after the SCWD, indicating that SCW conditions dramatically alter MoO₃ morphology. Initially, the MoO₃ particles were plate-like, with characteristic dimensions larger than 100 μ m. After 60 min SCW treatment, MoO₃ particles have a flower-like morphology with filaments with an average diameter of 74 nm (Fig. 9c). Consistent with this morphological change, the surface area of the HS-HD exposed MoO₃ sample was twice that of the virgin sample (Table 1). These observations are consistent with literature reports on the stability of MoO₃ at elevated temperatures [52,54,72,75–77]

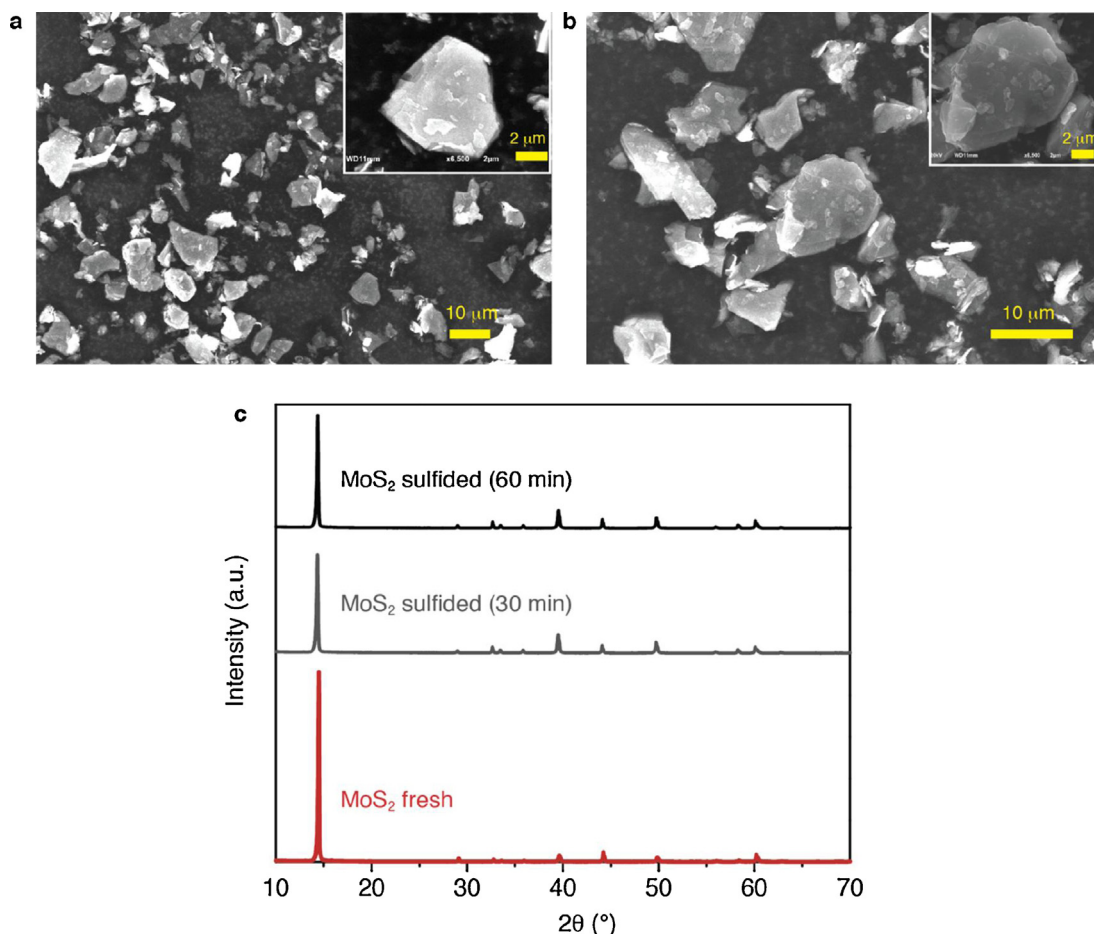


Fig. 8. (a and b) SEM images of fresh and sulfided MoS₂, respectively; insets are high magnification micrographs (scale bars are 2 μm). (c) XRD spectra of fresh and sulfided MoS₂ after SCW sulfurization of HS-HD model feed for 30 min and 60 min at 400 °C and 25 MPa.

Despite the formation of a higher surface area sulfided catalyst during SCW desulfurization treatment, MoO₃ was ineffective at reducing DBT content of the DBT-HD feed. We surmise that MoO₃ is incapable of generating sufficient H₂S from DBT to become an active sulfided catalyst. Since real feeds contain a suite of sulfur compounds, future work should be performed to test the activity of MoO₃ for desulfurization of model feeds containing mixtures of sulfides (to produce H₂S and sulfide the catalyst) and more refractory compounds.

3.3.3. Characterization of ZnO

As anticipated, ZnO is readily sulfided during exposure to the HS-HD conditions. The Supporting information provides SEM, XPS, and XRD results for the ZnO catalyst, showing that 62% of the surface becomes converted to ZnS whereas the bulk material contained 15% wurtzite ZnS. Fresh ZnO consisted of nano-scale spherical particles with an average diameter less than 100 nm (Fig. 10a and b). After SCW treatment, ZnO particles appeared more porous and were smaller in size (Fig. 10c and d). Interestingly, ZnO was found to be the most active catalyst for DBT removal, despite its low stability in the sulfur-rich environment. We are not aware of any literature reports on the use of ZnS for desulfurization, and – given the low cost and abundance of ZnO – the observation of DBT removal in the presence of ZnO/ZnS merits further study. Since the ZnO/ZnS catalyst may be sacrificial, specific effort should be addressed at regenerating the catalyst and re-evaluating its activity.

4. Discussion

SCW has some potential benefits as a hydrogen-free alternative to HDS. Table 4 summarizes the primary desulfurization methods that have been described in the literature. Of these, HDS will likely be the primary sulfur removal technology for the foreseeable future. This prediction reflects both the performance of HDS, the capital investment in HDS infrastructure, and the industrial know-how for running HDS processes smoothly [2,72–75]. Nonetheless, alternative processes are desired either for specific sites (e.g., remote locations where providing hydrogen may not be feasible) or as complementary technologies used in tandem with HDS.

As described in the Introduction, the main alternatives to HDS include ODS, ACS, BDS, and SCW. The advantages of ODS, ADS, and BDS lie in their ability to remove sulfur without the use of supplied hydrogen and at mild process conditions (<100 °C and 1 bar pressure is typical). ODS has been shown to be particularly effective for the dibenzothiophene compounds that are recalcitrant to HDS [76–78]. However, the oxidant required for ODS suggests that it might be best suited as a polishing step, for instance to reduce sulfur content below 15 ppm_w after an initial HDS step. Additionally, ODS removes the entire sulfur compound – not just the sulfur component as occurs in HDS – and the subsequent loss in hydrocarbons makes ODS impractical for whole crudes unless ODS can be coupled with a second C–S bond breaking step. Overall hydrogen consumption increases non-linearly with desulfurization level,

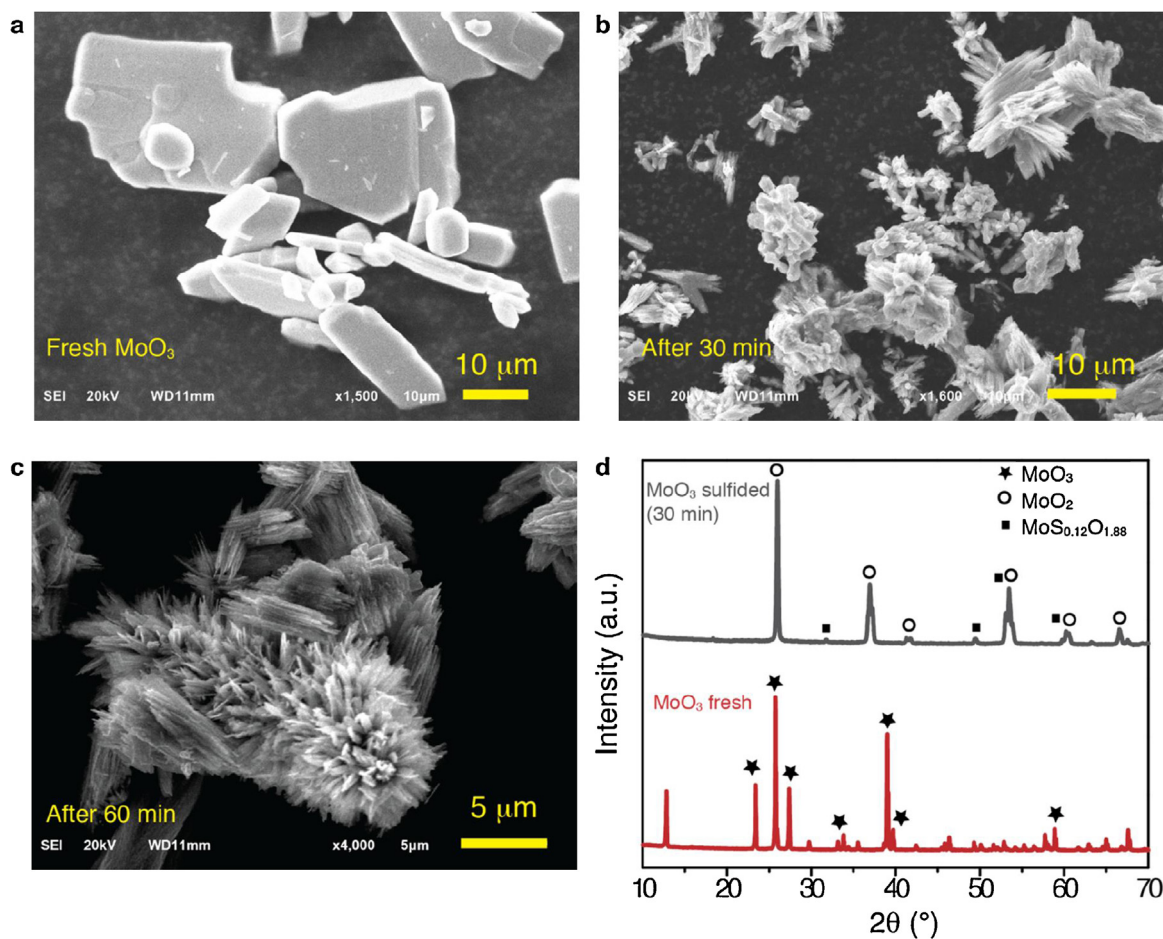


Fig. 9. SEM micrographs of (a) fresh MoO_3 ; (b) MoO_3 after 30 min SCW desulfurization of HS-HD; (c) MoO_3 after 60 min SCW desulfurization of HS-HD. (d) XRD spectra of MoO_3 before and after 30 min SCW desulfurization of HS-HD at 400°C and 25 MPa [Feed: 3 wt% S (HS) in HD (1:1 wt/wt of oil/water at room temperature)].

indicating that a tandem HDS-ODS approach might lead to an overall reduction in operating costs.

Like ODS, ADS is most effective for thiophenic sulfur compounds that are refractory to HDS [12–16]. For ADS a major limitation is the low sulfur capacity of most sorbents – on the order of mg per gram of sorbent [12,13,79]. Also like ODS, ADS results in loss of entire sulfur compounds. Therefore, using ADS to achieve deep desulfurization of whole crude oil would require extremely large sorbent quantities and result in substantial oil recovery losses. For these reasons, ADS may be better suited as a polishing step performed

following HDS. Accordingly, ADS has received specific attention for sulfur removal from refined fuels like diesel and jet fuels, especially as a portable technology to support fuel cell power generation [79–82].

BDS, which is sometimes viewed as a specific type of ODS process, utilizes air to oxidize sulfur compounds ultimately to water-soluble sulfates, thereby overcoming two of the main perceived disadvantages of ODS, chiefly oxidant costs and carbon losses [83–86]. Unfortunately, to date BDS has only achieved modest desulfurization rates and is poorly optimized for removal of

Table 4
Comparison of sulfur removal technology reported in literature.

Technology	Required auxiliary chemicals	Reaction conditions	Catalyst	Notes	Likely use	Ref.
HDS	Hydrogen	$300\text{--}400^\circ\text{C}$, >30 bar	Sulfided Co Mo	Hydrogen usage is a primary refinery operating cost	Primary sulfur removal method	[2,76,77]
ADS	None	1 bar, temperature as low as 25°C	None	Low adsorbent capacities (mg per g)	Sulfur polishing step	[12–16]
ODS	Oxidant	$<100^\circ\text{C}$, 1 bar	Polyoxometalates, ionic liquids, and many others	Selectivity to sulfur oxidation is a challenge	Sulfur polishing step	[5–8]
BDS	Oxidant	1 bar, $<50^\circ\text{C}$	Microorganism	Typically achieves very slow rates	Pre-treatment	[17–19]
SCW	Water	$>350^\circ\text{C}$, 230 bar	Under investigation	Best suited as a pre-treatment to reduce the burden on HDS	Pre-treatment	[20–24,89–95]

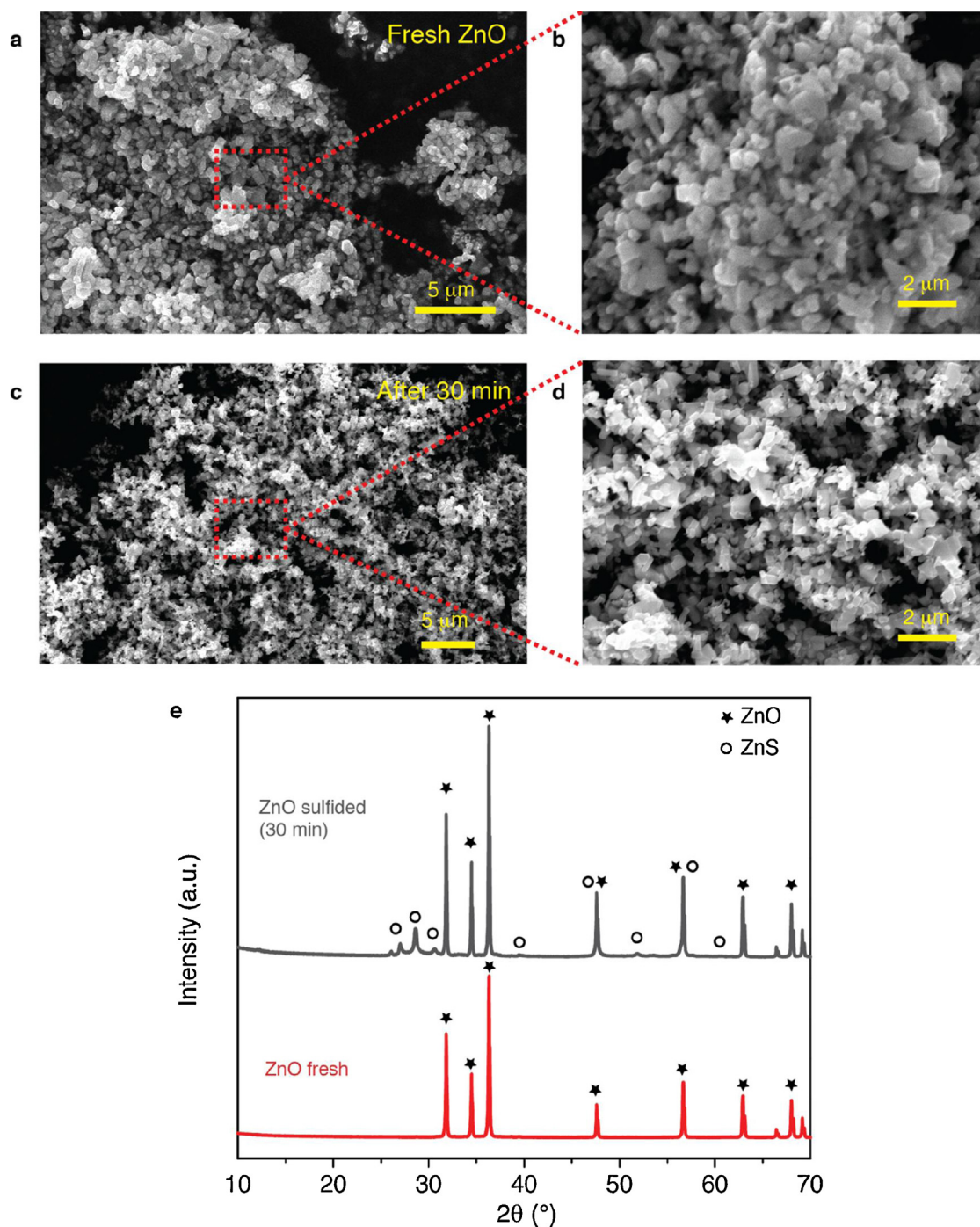


Fig. 10. (a and b) low and high magnification SEM images of fresh ZnO before SCWD exposure, respectively. (c and d) low and high magnification SEM images of sulfided ZnO after SCWD treatment of HS-HD feed for 30 min at 400 °C and 25 MPa. (e) XRD spectra of ZnO catalyst before and after SCW desulfurization of HS-HD model feed for 30 min at 400 °C and 25 MPa, indicating that after SCWD, 15% of bulk ZnO transformed into würtzite ZnS.

dibenzothiophene compounds. For this reason, BDS might be best deployed as a crude oil pre-treatment technology [83–86].

Like BDS, SCWDS may have the most potential as a pre-treatment technology. Unlike BDS, SCW conditions are severe (>400 °C and 22 MPa) but desulfurization rates are much faster than for BDS. Like BDS, our results and the results of others [20,27–29] indicate that SCW treatment alone cannot remove dibenzothiophene compounds. Instead, the advantage of SCW treatment is that many less refractory sulfur compounds can be removed without addition of hydrogen, thereby reducing the burden on downstream

processes. Prior work in this field has also shown that SCW treatment results in minimal coke formation – therefore, it has potential advantages over fluidized catalytic cracking, a process which produces large amounts of coke [21,22,87,88]. Finally, substantial work with bitumen and other real feeds [20–24,88–94] show that SCW treatment decrease viscosity and density while increasing the potential yield of middle distillates. Based on these factors, SCW treatment might be best utilized as a pre-treatment technology to complement HDS or as a means to increase the value of particularly sour or heavy feeds, such as Arabian Heavy. To further improve

desulfurization performance, the SCW treatment might be combined with partial oxidation to liberate CO and a water–gas–shift catalyst to produce hydrogen inside the reaction zone [36]. The disadvantage of the partial oxidation approach is that a percentage of the carbon present in the crude oil would be sacrificed; detailed mass balance and kinetic rate information would be required to evaluate the feasibility of the partial oxidation approach for a given feed.

Addition of low-cost catalysts might improve the sulfur removal performance of the SCW process, making it more economically attractive. Here, we have shown that MoS₂ reduces AH sulfur content more than SCW treatment alone and that MoS₂ causes a dramatic shift in AH sulfur composition. Our future work in this area will therefore be focused on testing more active sulfide catalysts – e.g., MoS₂ or CoMo [95–100] nanoparticles supported on stable supports such as TiO₂ or ZrO₂ [97–99,101–103].

5. Conclusion

In summary, we performed SCW desulfurization in the absence of an external hydrogen source, with and without a catalyst, for three feeds: Arabian heavy (AH) whole crude oil containing 3 wt% sulfur; a HS-HD model feed containing 3 wt% sulfur; and a DBT-HD model feed containing 0.1 wt% sulfur. ZnO, MoO₃ and MoS₂ were evaluated for desulfurization activity and stability in SCW. We found that SCW alone (without a catalyst) removes 6–7% of the sulfur present in AH crude oil and addition of MoS₂ to this system, increases sulfur removal to ~12%. GC-SCD analysis of the hydrocarbon product indicated a shift in the sulfur distribution to lighter sulfur compounds. For the HS-HD feed, HS conversion was high (~85%) in SCW alone. MoS₂ catalyst showed modest desulfurization activity for HS; whereas, the MoO₃ and ZnO catalysts did not improve sulfur removal from HS-HD feed. More interestingly, MoS₂ reduced the concentrations of secondary sulfur compounds retained in the hydrocarbon product, either by altering the reaction mechanism or by promoting decomposition of the secondary compounds themselves. For the DBT-HD feed, we observed 25% DBT decomposition in the presence of the ZnO catalyst, a potentially important result. We did in fact observe an H₂S product; however, our analytical techniques were unable to close the sulfur balance. Mass balance calculations suggest that chemical reaction should be the dominant DBT removal mechanism, though adsorption to the ZnO surface may also contribute.

We characterized bulk and surface properties of fresh and used catalysts for the HS-HD model system by XRD, SEM, and XPS. Consistent with our expectations, we found that MoS₂ preserves its chemistry and crystallographic structure during the SCW treatment; whereas MoO₃ and ZnO undergo major structural and composition changes, primarily due to sulfidation reactions. Further work is required to quantify coke formation and catalyst deactivation and to evaluate regeneration of the ZnS materials.

In summary, these results provide new insight into catalyst activity and stability for the SCW desulfurization and open the door to future studies on advancing SCW as a potential route of refinery desulfurization in the absence of an external hydrogen source.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.08.018>.

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